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(54) Porous materials

(57) Porous dielectric materials having low dielectric constants > 30% porosity and a closed cell pore structure are disclosed along with methods of preparing the materials. Such materials are particularly suitable for use in the manufacture of electronic devices.

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material is $\geq 30\%$ porous; and wherein the mean particle size of the plurality of porogen particles is selected to provide a closed cell pore structure.

[0012] In a fourth aspect, the present invention provides a method of manufacturing a porous organo polysilica dielectric material suitable for use in electronic device manufacture including the steps of: a) dispersing a plurality of removable polymeric porogen particles in a B-staged organo polysilica dielectric material; b) curing the B-staged organo polysilica dielectric material to form a dielectric matrix material without substantially degrading the porogen particles; c) subjecting the organo polysilica dielectric matrix material to conditions which at least partially remove the porogen to form a porous dielectric material without substantially degrading the organo polysilica dielectric material; wherein the porogen is substantially compatible with the B-staged organo polysilica dielectric material and wherein the porogen includes as polymerized units at least one compound selected from silyl containing monomers or poly(alkylene oxide) monomers; wherein the dielectric material is $\geq 30\%$ porous; and wherein the mean particle size of the plurality of porogen particles is selected to provide a closed cell pore structure.

[0013] In a fifth aspect, the present invention provides a method of preparing an integrated circuit with a closed cell porous film including the steps of: a) depositing on a substrate a layer of a composition including B-staged organo polysilica dielectric material having polymeric porogen dispersed therein; b) curing the B-staged organo polysilica dielectric material to form an organo polysilica dielectric matrix material without substantially removing the porogen; c) subjecting the organo polysilica dielectric matrix material to conditions which at least partially remove the porogen to form a porous organo polysilica dielectric material layer without substantially degrading the organo polysilica dielectric material; d) patterning the porous dielectric layer; e) depositing a metallic film onto the patterned porous dielectric layer; and f) planarizing the film to form an integrated circuit; wherein the porogen is substantially compatible with the B-staged organo polysilica dielectric material and wherein the porogen includes as polymerized units at least one compound selected from silyl containing monomers or poly(alkylene oxide) monomers; and wherein the dielectric material is $\geq 30\%$ porous.

[0014] In a sixth aspect, the present invention provides a method of preparing an integrated circuit with a closed cell porous film including the steps of: a) depositing on a substrate a layer of a composition including B-staged dielectric material having a plurality of polymeric porogens dispersed therein; b) curing the B-staged dielectric material to form a dielectric matrix material without substantially removing the porogens; c) subjecting the dielectric matrix material to conditions which at least partially remove the porogens to form a porous dielectric material layer without substantially degrading the dielectric material; d) patterning the porous dielectric layer; e) depositing a metallic film onto the patterned porous dielectric layer; and f) planarizing the film to form an integrated circuit; wherein the porogen is substantially compatible with the B-staged dielectric material; and wherein the dielectric material is $\geq 30\%$ porous; and wherein the mean particle size of the porogens is selected to provide a closed cell pore structure.

[0015] In a seventh aspect, the present invention provides an integrated circuit including a porous dielectric material wherein the porous dielectric material $\geq 30\%$ porous; wherein the pores are substantially non-interconnected; and wherein the mean particle size of the pores is selected to provide a closed cell pore structure.

[0016] In an eighth aspect, the present invention provides an electronic device including a porous dielectric layer free of an added cap layer, wherein the porous dielectric layer has $\geq 30\%$ porosity.

Brief Description of the Drawing

[0017] FIG. 1 illustrates a modified Randles circuit.

[0018] FIG. 2 illustrates a test cell for determining the pore structure of porous thin film materials.

Detailed Description of the Invention

[0019] As used throughout this specification, the following abbreviations shall have the following meanings, unless the context clearly indicates otherwise: °C = degrees centigrade; μm = micron; UV = ultraviolet; ppm = parts per million; nm = nanometer; S/m = Siemens per meter; g = gram; wt% = weight percent; Hz = hertz; kHz = kilohertz; mV = millivolts; MIAK = methyl iso-amyl ketone; MIBK = methyl iso-butyl ketone; PMA = poly(methyl acrylate); CyHMA = cyclohexylmethacrylate; EG = ethylene glycol; DPG = dipropylene glycol; DEA = diethylene glycol ethyl ether acetate; BzA = benzylacrylate; BzMA = benzyl methacrylate; MAPS = MATS = (trimethoxysilyl)propylmethacrylate; PETTA = pentacrythriol tetra/triacetate; PPG4000DMA = polypropyleneglycol 4000 dimethacrylate; DPEPA = dipentaerythriol pentaacrylate; TMSMA = trimethylsilyl methacrylate; MOPTSOMS = methacryloxypropylbis(trimethylsiloxy)methylsilane; MOPMDMOS = 3-methacryloxypropylmethyldimethoxysilane; TAT = triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione; IBOMA isobornyl methacrylate; PGMEA = propyleneglycol monomethylether acetate; and PGDMA = propyleneglycol dimethacrylate; PPODMST = poly(propylene oxide), bis(dimethoxymethylsilyl); TMOPTMA = trimethylolpropane trimethacrylate; TMOPTA = trimethylolpropane triacrylate; BPEPDMS = bis polyetherpolydimethylsilane; PPGMEA260 = poly(propylene glycol) methyl ether acrylate having a molecular weight of about 260; PPGMEA475 = poly(propylene

silsesquioxane; alkyl/aryl silsesquioxane mixtures such as a mixture of methyl silsesquioxane and phenyl silsesquioxane; and mixtures of alkyl silsesquioxanes such as methyl silsesquioxane and ethyl silsesquioxane. B-staged silsesquioxane materials include homopolymers of silsesquioxanes, copolymers of silsesquioxanes or mixtures thereof. Such dielectric materials are generally commercially available or may be prepared by known methods.

[0027] It is preferred that the organo polysilica is a silsesquioxane, and more preferably methyl silsesquioxane, ethyl silsesquioxane, propyl silsesquioxane, iso-butyl silsesquioxane, tert-butyl silsesquioxane, phenyl silsesquioxane or mixtures thereof. Particularly useful silsesquioxanes include mixtures of hydrido silsesquioxanes with alkyl, aryl or alkyl/aryl silsesquioxanes. Other particularly useful silsesquioxanes include combinations of alkyl or aryl silsesquioxanes with tetra(C₁-C₆)alkylorthosilicates such as tetraethylorthosilicate, or copolymers or composites thereof. Exemplary combinations of alkyl silsesquioxanes with tetra(C₁-C₆)alkylorthosilicate are disclosed in U.S. Patent No. 4,347,609 (Fukuyama et al.). Also suitable are cohydrolysates of tetra(C₁-C₆)alkylorthosilicates or silicon tetrachloride with a compound of the formula RSiX₃, wherein R is selected from (C₁-C₆)alkyl or aryl; and X is selected from halo, (C₁-C₄)alkoxy or acyloxy. Typically, the silsesquioxanes useful in the present invention are used as oligomeric materials, generally having from about 3 to about 10,000 repeating units.

[0028] Other suitable silsesquioxane compositions include, but are not limited to: hydrogen silsesquioxane, alkyl silsesquioxane such as methyl silsesquioxane, aryl silsesquioxane such as phenyl silsesquioxane, and mixtures thereof, such as alkyl/hydrogen, aryl/hydrogen, alkyl/aryl silsesquioxane or alkyl/aryl/hydrido silsesquioxane. It is preferred that the dielectric material comprises a silsesquioxane, more preferably a combination of a silsesquioxane with a tetra (C₁-C₆)alkylorthosilicates, and still more preferably a combination of methyl silsesquioxane with tetraethylorthosilicate.

[0029] Also provided by the present invention is a closed cell porous organo polysilica dielectric film suitable for use in electronic device manufacture, the porous organo polysilica dielectric film having greater than or equal to 30% porosity. The present invention further provides a closed cell porous film comprising hydrogen silsesquioxane as monomer units for use in electronic device manufacture, the porous film having greater than or equal to 30% porosity.

[0030] It will be appreciated that a mixture of dielectric materials may be used, such as two or more organo polysilica dielectric materials or a mixture of an organo polysilica dielectric matrix material with one or more other dielectric matrix materials, i.e. not an organo polysilica dielectric matrix material. Suitable other dielectric matrix materials include, but are not limited to, inorganic matrix materials such as carbides, oxides, nitrides and oxyfluorides of silicon, boron, or aluminum; and organic matrix materials such as benzocyclobutenes, poly(aryl esters), poly(ether ketones), polycarbonates, polyimides, fluorinated polyimides, polynorbornenes, poly(arylene ethers), polyaromatic hydrocarbons, such as polynaphthalene, polyquinoxalines, poly(perfluorinated hydrocarbons) such as poly(tetrafluoroethylene), and polybenzoxazoles.

[0031] It is preferred that when a mixture of an organo polysilica dielectric matrix material and another dielectric matrix material is used, the organo polysilica dielectric matrix material is present as a predominant component. It is further preferred that the organo polysilica dielectric matrix material in such admixtures is methyl silsesquioxane, phenyl silsesquioxane or mixtures thereof.

[0032] Porous dielectric materials having a wide variety of porosities can be prepared according to the present invention. Typically, the porous materials have a porosity of $\geq 30\%$ by volume, preferably $\geq 35\%$, more preferably $\geq 40\%$, and even more preferably $\geq 45\%$. Porosities of 50% can also be achieved according to the present invention. Such porosity is a measure of the total volume of pores in the dielectric material.

[0033] The pore structure of the porous thin film dielectric materials of the present invention can be determined by a variety of methods. Preferably, an electrochemical test is used to measure an electrical property of the material, such as impedance, conductivity and the like. Particularly suitable is electrochemical impedance spectroscopy ("EIS").

[0034] Dielectric films typically have a very high impedance. When the film matrix contains open channels, a decrease in impedance is recorded as solvent and ions penetrate the film. When monitored by EIS, these phenomena can evaluate the porosity of the dielectric film.

[0035] In an EIS experiment, a variable frequency alternating current ("AC") potential is applied to a system and the current is measured. The response follows Ohm's law, ($E = IZ$) where the current ("I") and the impedance ("Z") are represented by complex numbers. The frequency-independent impedance is related to resistance ("R") and the frequency-dependent impedance is related to capacitance ("C"). When the data are computer modeled, a modified Randles circuit adequately describes the sample's behavior. A suitable Randles circuit is shown in FIG. 1, where R_{ct} is the resistance for the charge transfer and C_{dl} is the double layer capacitance. This model accounts for electrode interfacial reactions (" \bar{R}_i ") as well as the sample's resistance (" R_{po} ") and sample's capacitance (" C_c ").

[0036] This R_{po} resistance is an indication of the rate of mass transport of ions into ionically conducting low resistive channels in the film. Values of R_{po} are, therefore, related to the film's ionic conductivity, according to the formula

$$R_{po} = \rho d = (\sigma)^{-1} = (\mu c n z)^{-1}$$

al., Properties of Polymers. Their Estimation and Correlation with Chemical Structure, Elsevier Scientific Publishing Co., 1976; Olabisi et al., Polymer-Polymer Miscibility, Academic Press, NY, 1979; Coleman et al., Specific Interactions and the Miscibility of Polymer Blends, Technomic, 1991; and A. F. M. Barton, CRC Handbook of Solubility Parameters and Other Cohesion Parameters, 2nd Ed., CRC Press, 1991. Delta h is a hydrogen bonding parameter of the material and delta v is a measurement of both dispersive and polar interaction of the material. Such solubility parameters may either be calculated, such as by the group contribution method, or determined by measuring the cloud point of the material in a mixed solvent system consisting of a soluble solvent and an insoluble solvent. The solubility parameter at the cloud point is defined as the weighted percentage of the solvents. Typically, a number of cloud points are measured for the material and the central area defined by such cloud points is defined as the area of solubility parameters of the material.

[0045] When the solubility parameters of the porogen and dielectric matrix material are substantially similar, the porogen will be compatible with the dielectric matrix material and phase separation and/or aggregation of the porogen is less likely to occur. It is preferred that the solubility parameters, particularly delta h and delta v, of the porogen and dielectric matrix material are substantially matched. It will be appreciated by those skilled in the art that the properties of the porogen that affect the porogen's solubility also affect the compatibility of that porogen with the B-staged dielectric material. It will be further appreciated by those skilled in the art that a porogen may be compatible with one B-staged dielectric material, but not another. This is due to the difference in the solubility parameters of the different B-staged dielectric materials,

[0046] The compatible, i.e., optically transparent, compositions of the present invention do not suffer from agglomeration or long range ordering of porogen materials, i.e. the porogen is substantially uniformly dispersed throughout the B-staged dielectric material. Thus, the porous dielectric materials resulting from removal of the porogen have substantially uniformly dispersed pores. Such substantially uniformly dispersed, very small pores are very effective in reducing the dielectric constant of the dielectric materials.

[0047] The porogens used to form the present highly porous dielectric materials have a particle size selected to maintain a closed cell structure at a given porosity. Too small a pore size may result in an open cell, or interconnected, pore structure for a give porosity of the dielectric material. A porogen having a particular particle size that provides a closed cell structure at 30% porosity may provide an open cell pore structure at higher levels of porosity. For example, for porous dielectric materials having $\geq 30\%$ porosity, the porogens must have a particle size greater than 2.5 nm. For 30% porosity, it is preferred that the porogen has a particle size ≥ 2.75 nm, and preferably ≥ 3 nm. Typically, for dielectric materials having a porosity of 30% to 35%, a porogen having a particle size in the range of 2.75 to 4 nm is selected, and preferably 3 to 3.5 nm. For dielectric materials having a porosity of 35% to 40%, a porogen having a particle size in the range of 3.5 to 8 nm, and preferably 4 to 7 nm, is selected. For dielectric materials having a porosity of 40% to 45%, a porogen having a particle size in ≥ 5 nm is selected, preferably 5 to 15 nm, more preferably 5 to 11 nm, and even more preferably 5 to 7 nm. If the size of the porogen is too large, the resulting pores in the dielectric material will be too large to be suitable for advanced electronic devices having very narrow linewidths. Thus, there is an optimum range of pore sizes useful for providing porous dielectric materials having closed cell pore structures.

[0048] A wide variety of porogens are suitable for use in the present invention. The porogen polymers are typically cross-linked particles and have a molecular weight and particle size suitable for use as a modifier in advanced interconnect structures in electronic devices. Typically, the useful particle size range for such applications is up to about 100 nm, such as that having a mean particle size in the range of about 0.5 to about 100 nm. However, for the present closed cell porous dielectric materials, it is preferred that the mean particle size is in the range of about 2.75 to about 20 nm, more preferably from about 3 to about 15 nm, and most preferably from about 3 nm to about 10 nm. An advantage of the present process is that the size of the pores formed in the dielectric matrix are substantially the same size, i.e., dimension, as the size of the removed porogen particles used. Thus, the porous dielectric material made by the process of the present invention has substantially uniformly dispersed pores with substantially uniform pore sizes having a mean pore size in the range of from 2.75 to 20 nm, preferably 3 to 15 nm, and more preferably 3 and 10 nm.

[0049] The polymers suitable for use as porogens in the present invention are derived from ethylenically or acetylenically unsaturated monomers and are removable, such as by the unzipping of the polymer chains to the original monomer units which are volatile and diffuse readily through the host matrix material. By "removable" is meant that the polymer particles depolymerize, degrade or otherwise break down into volatile components which can then diffuse through the host dielectric matrix film. Suitable unsaturated monomers include, but are not limited to: (meth)acrylic acid, (meth)acrylamides, alkyl (meth)acrylates, alkenyl (meth)acrylates, aromatic (meth)acrylates, vinyl aromatic monomers, nitrogen-containing compounds and their thio-analogs, and substituted ethylene monomers.

[0050] Typically, the alkyl (meth)acrylates useful in the present invention are (C₁-C₂₄) alkyl (meth)acrylates. Suitable alkyl (meth)acrylates include, but are not limited to, "low cut" alkyl (meth)acrylates, "mid cut" alkyl (meth)acrylates and "high cut" alkyl (meth)acrylates.

[0051] "Low cut" alkyl (meth)acrylates are typically those where the alkyl group contains from 1 to 6 carbon atoms. Suitable low cut alkyl (meth)acrylates include, but are not limited to: methyl methacrylate ("MMA"), methyl acrylate,

invention include, but are not limited to: vinylpyridines such as 2-vinylpyridine or 4-vinylpyridine; lower alkyl (C_1 - C_8) substituted N-vinyl pyridines such as 2-methyl-5-vinyl-pyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2,3-dimethyl-5-vinyl-pyridine, and 2-methyl-3-ethyl-5-vinylpyridine; methyl-substituted quinolines and isoquinolines; N-vinylcaprolactam; N-vinylbutyrolactam; N-vinylpyrrolidone; vinyl imidazole; N-vinyl carbazole; N-vinyl-succinimide; (meth)acrylonitrile; *o*-, *m*-, or *p*-aminostyrene; maleimide; N-vinyl-oxazolidone; N,N-dimethyl aminocethyl-vinyl-ether; ethyl-2-cyano acrylate; vinyl acetonitrile; N-vinylphthalimide; N-vinyl-pyrrolidones such as N-vinyl-thio-pyrrolidone, 3-methyl-1-vinyl-pyrrolidone, 4-methyl-1-vinyl-pyrrolidone, 5-methyl-1-vinyl-pyrrolidone, 3-ethyl-1-vinyl-pyrrolidone, 3-butyl-1-vinyl-pyrrolidone, 3,3-dimethyl-1-vinyl-pyrrolidone, 4,5-dimethyl-1-vinyl-pyrrolidone, 5,5-dimethyl-1-vinyl-pyrrolidone, 3,3,5-trimethyl-1-vinyl-pyrrolidone, 4-ethyl-1-vinyl-pyrrolidone, 5-methyl-5-ethyl-1-vinyl-pyrrolidone and 3,4,5-trimethyl-1-vinyl-pyrrolidone; vinyl pyrroles; vinyl anilines; and vinyl piperidines.

[0061] The substituted ethylene monomers useful as unsaturated monomers in the present invention include, but are not limited to: vinyl acetate, vinyl formamide, vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, vinylidene fluoride and vinylidene bromide.

[0062] When the dielectric material is an organo polysilica material, it is preferred that polymeric porogens include as polymerized units at least one compound selected from silyl containing monomers or poly(alkylene oxide) monomers. Such silyl containing monomers or poly(alkylene oxide) monomers may be used to form the uncrosslinked polymer, used as the crosslinker, or both. Any monomer containing silicon may be useful as the silyl containing monomers in the present invention. The silicon moiety in such silyl containing monomers may be reactive or unreactive. Exemplary "reactive" silyl containing monomers include those containing one or more alkoxy or acetoxy groups, such as, but not limited to, trimethoxysilyl containing monomers, triethoxysilyl containing monomers, methyl dimethoxysilyl containing monomers, and the like. Exemplary "unreactive" silyl containing monomers include those containing alkyl groups, aryl groups, alkenyl groups or mixtures thereof, such as but are not limited to, trimethylsilyl containing monomers, triethylsilyl containing monomers, phenyldimethylsilyl containing monomers, and the like. Polymeric porogens including silyl containing monomers as polymerized units are intended to include such porogens prepared by the polymerization of a monomer containing a silyl moiety. It is not intended to include a linear polymer that contains a silyl moiety only as end capping units.

[0063] Suitable silyl containing monomers include, but are not limited to, vinyltrimethylsilane, vinyltriethylsilane, vinyltrimethoxysilane, vinyltriethoxysilane, γ -trimethoxysilylpropyl (meth)acrylate, divinylsilane, trivinylsilane, dimethyl-divinylsilane, divinylmethylsilane, methyltrivinylsilane, diphenyldivinylsilane, divinylphenylsilane, trivinylphenylsilane, divinylmethylphenylsilane, tetravinylsilane, dimethylvinylsiloxane, poly(methylvinylsiloxane), poly(vinylhydrosiloxane), poly(phenylvinylsiloxane), allyloxy-tert-butyl dimethylsilane, allyloxytrimethylsilane, allyltriethoxysilane, allyltriisopropylsilane, allyltrimethoxysilane, allyltrimethylsilane, allyltriphenylsilane, diethoxy methylvinylsilane, diethyl methylvinylsilane, dimethyl ethoxyvinylsilane, dimethyl phenylvinylsilane, ethoxy diphenylvinylsilane, methyl bis(trimethylsilyloxy)vinylsilane, triacetoxyvinylsilane, triethoxyvinylsilane, triethylvinylsilane, triphenylvinylsilane, tris(trimethylsilyloxy)vinylsilane, vinyloxytrimethylsilane and mixtures thereof.

[0064] The amount of silyl containing monomer useful to form the porogens of the present invention is typically from about 1 to about 99 %wt, based on the total weight of the monomers used. It is preferred that the silyl containing monomers are present in an amount of from 1 to about 80 %wt, and more preferably from about 5 to about 75 %wt.

[0065] Suitable poly(alkylene oxide) monomers include, but are not limited to, poly(propylene oxide) monomers, poly(ethylene oxide) monomers, poly(ethylene oxide/propylene oxide) monomers, poly(propylene glycol) (meth)acrylates, poly(propylene glycol) alkyl ether (meth)acrylates, poly(propylene glycol) phenyl ether (meth)acrylates, poly(propylene glycol) 4-nonylphenol ether (meth)acrylates, poly(ethylene glycol) (meth)acrylates, poly(ethylene glycol) alkyl ether (meth)acrylates, poly(ethylene glycol) phenyl ether (meth)acrylates, poly(propylene/ethylene glycol) alkyl ether (meth)acrylates and mixtures thereof. Preferred poly(alkylene oxide) monomers include trimethyloxypropane ethoxylate tri(meth)acrylate, trimethyloxypropane propoxylate tri(meth)acrylate, poly(propylene glycol) methyl ether acrylate, and the like. Particularly suitable poly(propylene glycol) methyl ether acrylate monomers are those having a molecular weight in the range of from about 200 to about 2000. The poly(ethylene oxide/propylene oxide) monomers useful in the present invention may be linear, block or graft copolymers. Such monomers typically have a degree of polymerization of from about 1 to about 50, and preferably from about 2 to about 50.

[0066] Typically, the amount of poly(alkylene oxide) monomers useful in the porogens of the present invention is from about 1 to about 99 %wt, based on the total weight of the monomers used. The amount of poly(alkylene oxide) monomers is preferably from about 2 to about 90 %wt, and more preferably from about 5 to about 80 %wt.

[0067] The silyl containing monomers and the poly(alkylene oxide) monomers may be used either alone or in combination to form the porogens of the present invention. It is preferred that the silyl containing monomers and the poly(alkylene oxide) monomers are used in combination. In general, the amount of the silyl containing monomers or the poly(alkylene oxide) monomers needed to compatibilize the porogen with the dielectric matrix depends upon the level of porogen loading desired in the matrix, the particular composition of the organo polysilica dielectric matrix, and the composition of the porogen polymer. When a combination of silyl containing monomers and the poly(alkylene oxide)

stantially removed. Typical methods of removal include, but are not limited to, chemical, exposure to heat or exposure to radiation, such as, but not limited to, UV, x-ray, gamma ray, alpha particles, neutron beam or electron beam. It is preferred that the matrix material is exposed to heat or UV light to remove the porogen.

[0076] The porogens of the present invention can be thermally removed under vacuum, nitrogen, argon, mixtures of nitrogen and hydrogen, such as forming gas, or other inert or reducing atmosphere. The porogens of the present invention may be removed at any temperature that is higher than the thermal curing temperature and lower than the thermal decomposition temperature of the organo polysilica dielectric matrix material. Typically, the porogens of the present invention may be removed at temperatures in the range of 150° to 500° C and preferably in the range of 250° to 425° C. Typically, the porogens of the present invention are removed upon heating for a period of time in the range of 1 to 120 minutes. An advantage of the porogens of the present invention is that 0 to 20% by weight of the porogen remains after removal from the organo polysilica dielectric matrix material.

[0077] In one embodiment, when a porogen of the present invention is removed by exposure to radiation, the porogen polymer is typically exposed under an inert atmosphere, such as nitrogen, to a radiation source, such as, but not limited to, visible or ultraviolet light. The porogen fragments generated from such exposure are removed from the matrix material under a flow of inert gas. The energy flux of the radiation must be sufficiently high to generate a sufficient number of free radicals such that porogen particle is at least partially removed. It will be appreciated by those skilled in the art that a combination of heat and radiation may be used to remove the porogens of the present invention.

[0078] In preparing the dielectric matrix materials of the present invention, a plurality of porogen particles described above are first dispersed within, or dissolved in, a B-staged dielectric material. Any amount of porogen may be combined with the B-staged dielectric materials according to the present invention. The amount of porogen used will depend on the particular porogen employed, the particular B-staged dielectric material employed, the extent of dielectric constant reduction desired in the resulting porous dielectric material, i.e. the particular porosity desired, and the mean pore size of the porogen particles. Typically, the amount of porogen used is in the range of from 30 to 50 wt%, based on the weight of the B-staged dielectric material, preferably from 30 to 45 wt%, and more preferably from 30 to 40 wt%. A particularly useful amount of porogen is in the range of from about 30 to about 35 wt%.

[0079] The porogens of the present invention may be combined with the B-staged dielectric material by any methods known in the art. Typically, the B-staged dielectric material is first dissolved in a suitable high boiling solvent, such as, but not limited to, methyl isobutyl ketone, diisobutyl ketone, 2-heptanone, γ -butyrolactone, ϵ -caprolactone, ethyl lactate, propyleneglycol monomethyl ether acetate, propyleneglycol monomethyl ether, diphenyl ether, anisole, n-amyl acetate, n-butyl acetate, cyclohexanone, N-methyl-2-pyrrolidone, N,N'-dimethylpropyleneurea, mesitylene, xylenes, or mixtures thereof, to form a solution. The porogen particles are then dispersed or dissolved within the solution. The resulting dispersion is then deposited on a substrate by methods known in the art, such as spin coating, spray coating or doctor blading, to form a film or layer.

[0080] After being deposited on a substrate, the B-staged dielectric material is then substantially cured to form a rigid, cross-linked dielectric matrix material without substantially removing the porogen particles. The curing of the dielectric material may be by any means known in the art including, but not limited to, heating to induce condensation or e-beam irradiation to facilitate free radical coupling of the oligomer or monomer units. Typically, the B-staged material is cured by heating at an elevated temperature, e.g. either directly, e.g. heated at a constant temperature such as on a hot plate, or in a step-wise manner. Typically, the dielectric material containing polymeric porogens is first annealed at a temperature of from about 200° to about 350° C, and then heated to a higher temperature, such as from about 400° to about 450° C to at least partially remove the porogens. Such curing conditions are known to those skilled in the art.

[0081] Once the B-staged dielectric material is cured, the film is subjected to conditions which remove the porogen without substantially degrading the organo polysilica dielectric matrix material, that is, less than 5% by weight of the dielectric matrix material is lost. Typically, such conditions include exposing the film to heat and/or radiation. It is preferred that the matrix material is exposed to heat or light to remove the porogen. To remove the porogen thermally, the dielectric matrix material can be heated by oven heating or microwave heating. Under typical thermal removal conditions, the polymerized dielectric matrix material is heated to about 350° to 400° C. It will be recognized by those skilled in the art that the particular removal temperature of a thermally labile porogen will vary according to composition of the porogen. Upon removal, the porogen polymer depolymerizes or otherwise breaks down into volatile components or fragments which are then removed from, or migrate out of, the dielectric matrix material yielding pores or voids, which fill up with the carrier gas used in the process. Thus, a porous dielectric material having voids is obtained, where the size of the voids is substantially the same as the particle size of the porogen. By "substantially the same" it is meant that the diameter of the pores is within 10% of the mean particle size of the porogens used. The resulting dielectric material having voids thus has a lower dielectric constant than such material without such voids.

[0082] The present invention provides a method of manufacturing a porous dielectric material suitable for use in electronic device manufacture including the steps of: a) dispersing a plurality of removable polymeric porogen particles in a B-staged dielectric material, b) curing the B-staged dielectric material to form a dielectric matrix material without

electro and electroless deposition, sputtering, or the like. Optionally, a metallic liner, such as a layer of nickel, tantalum, titanium, tungsten, or chromium, including nitrides or silicides thereof, or other layers such as barrier or adhesion layers, e.g. silicon nitride or titanium nitride, is deposited on the patterned and etched dielectric material.

[0089] In a fifth step of the process for integrated circuit manufacture, excess metallic material is removed, e.g. by planarizing the metallic film, so that the resulting metallic material is generally level with the patterned dielectric layer. Planarization is typically accomplished with chemical/mechanical polishing or selective wet or dry etching. Such planarization methods are well known to those skilled in the art.

[0090] It will be appreciated by those skilled in the art that multiple layers of dielectric material, including multiple layers of organo polysilica dielectric material, and metal layers may subsequently be applied by repeating the above steps. It will be further appreciated by those skilled in the art that the compositions of the present invention are useful in any and all methods of integrated circuit manufacture.

[0091] Thus, the present invention provides a method of preparing an integrated circuit with a closed cell porous film including the steps of: a) depositing on a substrate a layer of a composition including B-staged dielectric material having a plurality of polymeric porogens dispersed therein; b) curing the B-staged dielectric material to form a dielectric matrix material without substantially removing the porogens; c) subjecting the dielectric matrix material to conditions which at least partially remove the porogens to form a porous dielectric material layer without substantially degrading the dielectric material; d) patterning the porous dielectric layer; e) depositing a metallic film onto the patterned porous dielectric layer; and f) planarizing the film to form an integrated circuit; wherein the porogen is substantially compatible with the B-staged dielectric material; and wherein the dielectric material is $\geq 30\%$ porous; and wherein the mean particle size of the porogens is selected to provide a closed cell pore structure.

[0092] It is preferred that the dielectric material is an organo polysilica material. Thus, the present invention also provides a method of preparing an integrated circuit with a closed cell porous film including the steps of: a) depositing on a substrate a layer of a composition including B-staged organo polysilica dielectric material having polymeric porogen dispersed therein; b) curing the B-staged organo polysilica dielectric material to form an organo polysilica dielectric matrix material without substantially removing the porogen; c) subjecting the organo polysilica dielectric matrix material to conditions which at least partially remove the porogen to form a porous organo polysilica dielectric material layer without substantially degrading the organo polysilica dielectric material; d) patterning the porous dielectric layer; e) depositing a metallic film onto the patterned porous dielectric layer; and f) planarizing the film to form an integrated circuit; wherein the porogen is substantially compatible with the B-staged organo polysilica dielectric material and wherein the porogen includes as polymerized units at least one compound selected from silyl containing monomers or poly(alkylene oxide) monomers; and wherein the dielectric material is $\geq 30\%$ porous.

[0093] Also included in the present invention is an integrated circuit including a porous dielectric material wherein the porous dielectric material is $\geq 30\%$ porous; wherein the pores are substantially non-interconnected; and wherein the mean particle size of the pores is selected to provide a closed cell pore structure. It is preferred that the porous dielectric material is an organo polysilica material, and more preferably methylsilsesquioxane. It is further preferred that the dielectric material has a porosity $\geq 35\%$.

[0094] A still further advantage provided by the close cell pore structure of the present porous dielectric materials is that a cap layer for the porous dielectric layer is not needed. Such cap layers are typically applied directly to the porous dielectric layer and act as a barrier preventing intrusion for the next applied layer into the pores of the dielectric material. Thus, the present invention provides an electronic device including a porous dielectric layer free of an added cap layer/ wherein the porous dielectric layer has $\geq 30\%$ porosity.

[0095] The following examples are presented to illustrate further various aspects of the present invention, but are not intended to limit the scope of the invention in any aspect.

Example 1

[0096] A methyl silsesquioxane ("MeSQ") sample is prepared by combining a methyl silsesquioxane resin (0.80 g), with a plurality of porogen particles having as polymerized units PEGMEMA475/VTMOS/TMPTMA (80/10/10) in propylene glycol methyl ether acetate (1.33 g, 15 wt%) and propylene glycol methyl ether acetate (1.43 g). The mean particle size of the plurality of porogen particles is varied. The sample is deposited on a silicon wafer as a thin coating using spin casting. The thickness (estimated at $\sim 1.1 \mu\text{m}$) of the film is controlled by the duration and spin rate of spread cycle, drying cycle and final spin cycle. The wafer is processed at 150°C for 1 minute followed by heating in a PYREX™ container in an oven to 200°C under an argon atmosphere. The oxygen content of the container is monitored and is maintained below 5 ppm before heating of the sample. After 30 minutes at 200°C , the furnace is heated at a rate of 10°C per minute to a temperature of 420°C and is held for 60 minutes. The decomposition of the polymer particle is accomplished at this temperature without expansion of the polymer.

[0097] The above procedure is repeated using various levels of porogen.

Table 1 (continued)

Porogen Loading Level (%)	Porogen Particle Size (nm)	Calculated Wall Thickness (nm)	Interconnectivity
40	7	0.66	Close Cell
45	9	0.47	Open Cell
45	10	0.52	Close Cell
45 1	1	0.57	Close Cell

Example 7

[0104] The procedure of Example 1 is repeated using a plurality of porogen particles having a mean particle size of 3,5 nm.

Example 8

[0105] The interconnectivity of the porous films from Example 7 are measured by placing a PYREX™ glass ball joint complete with a rubber o-ring against the thin, porous dielectric layer deposited onto a conductive silicon wafer, having a resistivity ("R") = <0.02 Ohm-cm. The ball joint is held in place by a clamp and then an aqueous 10,000 ppm of copper (as copper nitrate) ICP standard solution in 5% nitric acid is charged into the ball joint. A platinum electrode is placed into the solution and then a second reference electrode is also inserted into the solution. The back side of the wafer, i.e. the side opposite the film, is also contacted with an electrode. A measuring or monitoring system is used to record the impedance spectra with a Solartron 1260 Gain/Phase Analyzer, EG&G Princeton Applied Research (PAR) 273 potentiostat/Galvanostat, and Zplot Impedance Software (available from Scribner Associates). Individual data files are fit to a modified Randles circuit, (Zsim Impedance software from Scribner Associates), and their impedance parameters are plotted and compared as a function of time.

[0106] The copper ICP standard solution is allowed to remain in contact with the film for 24 hours and the impedance is measured again. These values are compared to those for a non-porous film. Differences in conductivity values of less than 1 indicate closed cell pore structures. Differences in conductivity values of greater than 1 indicate open cell pore structures.

Experimental parameters:	
Frequency range	100 KHz to 0.5 Hz
Sine wave amplitude	10mV
DC Potential	1 volt
Points/decade	5

[0107] The porous films of Example 7 are analyzed using this electrochemical test. For each sample film, the impedance value is reduced to the resistance which is then normalized for each of the films by dividing by the film thickness. The results are reported in Table 2.

Table 2

Porogen Loading (%)	Conductivity (S/m)	Interconnectivity
0	0.017	Close Cell
20	0.214	Close Cell
22	0.205	Close Cell
24	0.159	Close Cell
26	0.298	Close Cell
28	0.136	Close Cell
30	0.543	Close Cell
35	0.439	Close Cell
40	1.771	Open Cell

[0108] From these data, it can be seen that when a 3.5 nm particle is used, closed cell pore structures having between

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layer has $\geq 30\%$ porosity

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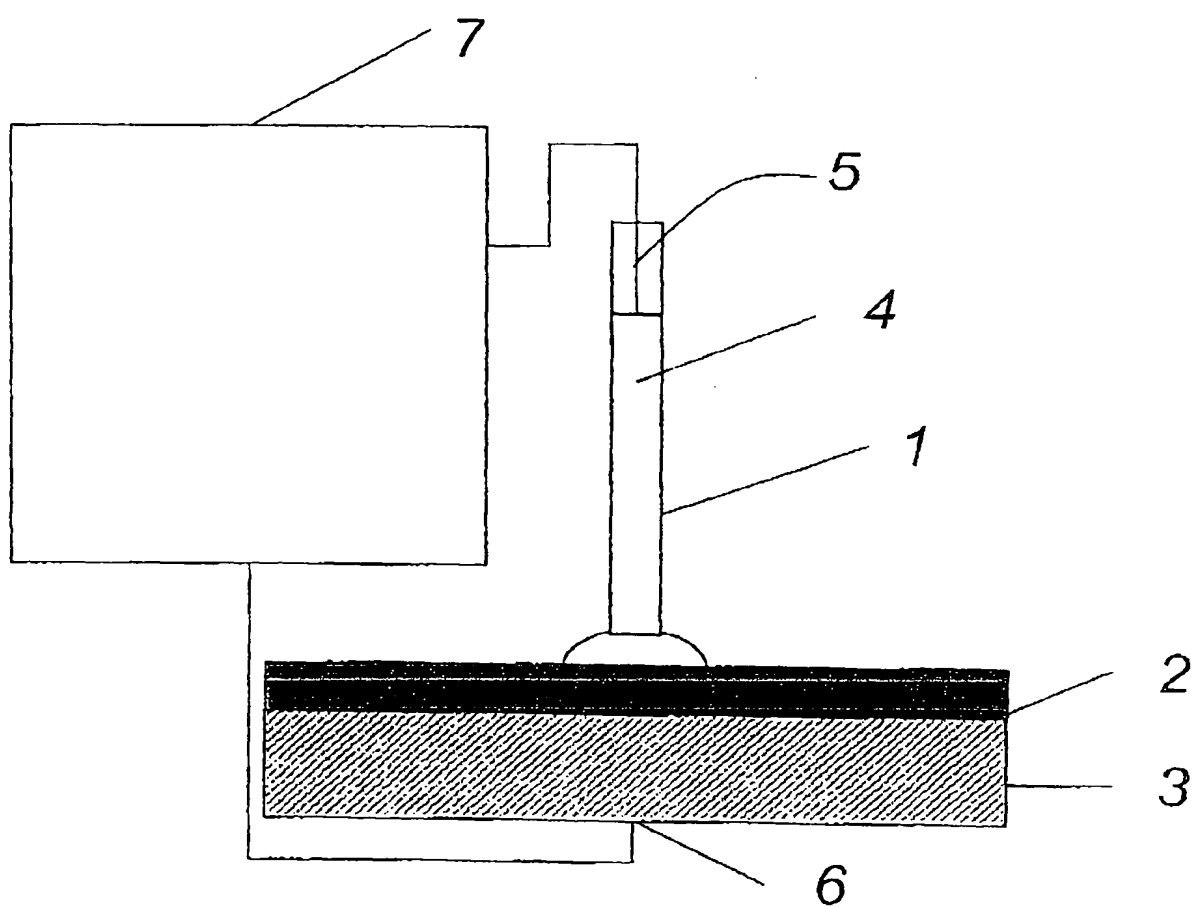
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FIG. 2



ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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